Tuesday, May 12
Facility-specific Workshops

APS Workshop 2
High-energy-resolution Inelastic X-ray Scattering

Location: Bldg. 401, Lecture Hall

Organizers: Ayman Said, Ahmet Alatas, and Bogdan M. Leu (APS)

The workshop is intended as a forum for researchers using high-energy-resolution inelastic x-ray scattering (IXS) to present recent results. Diverse areas of research, including superconductivity, geophysics, charge density waves, and quantum phase transitions, will be covered, as well as theoretical approaches to IXS. The timing of this workshop is ideal for us to update users on recent developments that took place on the HERIX instruments and to discuss new ideas.

8:30 – 8:35 Linda Young (Argonne National Laboratory)
Welcome & Introductory Remarks

8:35 – 8:45 Ayman Said (Argonne National Laboratory)
An Update about Sector 30

8:45 – 9:25 Frank Weber (Karlsruhe Institute of Technology)
Soft Phonon Mode and Wave Vector Dependent Electron-phonon Coupling at Charge-density Wave

9:25 – 10:05 Matthieu Le Tacon (Max Planck Institute for Solid State Research)
CDW and Electron-phonon Interaction in High-temperature Superconducting Cuprates

10:05 – 10:35 Break

10:35 – 11:15 Jiawang Hong (Oak Ridge National Laboratory)
Modeling the Phonon Dynamical Structure Factor S(Q,E) from First-principles Calculations: The Case Study of Thermoelectrics and Complex Oxides

11:15 – 12:00 Charles W. Myles
Clathrate Semiconductors: Novel, Open Framework, Crystalline Materials Based on Si, Ge, and Sn

12:00 – 1:30 Lunch

1:30 – 2:10 John Budai (Oak Ridge National Laboratory)
Comprehensive Scattering Studies of Microstructure, Anharmonic Phonons and Thermodynamics near the Metal-insulator Transition in VO_2

2:10 – 2:50 Jason Hancock (University of Connecticut)
Critical Soft Modes and Negative Thermal Expansion

2:50 – 3:20 Break

3:20 – 4:00	Jung-Fu Lin (The University of Texas at Austin) *High-pressure Acoustic Phonons and Elasticity of Iron Alloys and Oxides*
4:00 – 4:40	Nicholas Butch (NIST Center for Neutron Research) *Looking for Hidden Phonons in URu_2Si_2*
4:40 – 5:00	Wrap-up and concluding remarks
5:00	Adjourn

WK2

Soft Phonon Mode and Wave Vector Dependent Electron-phonon Coupling at Charge-density-wave Transitions

Frank Weber[1], Michael Maschek[1], Stephan Rosenkranz[2],Rolf Heid[1], Roland Hott[1],Dmitry Reznik[3], Goran Karapetrov[4], P. Giraldo-Gallo[5,7], I.R. Fisher[6,7], A. Alatas[8], and Ayman H. Said[8]

[1]Institute for Solid State Physics, Karlsruhe Institute for Technology, D-76021 Karlsruhe, Germany
[2]Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
[3]Department of Physics, University of Colorado at Boulder, Boulder, CO 80309
[4]Department of Physics, Drexel University, Philadelphia, PA 19104
[5]Geballe Laboratory for Advanced Physics and Department of Physics, Stanford University, CA 94305
[6]Geballe Laboratory for Advanced Physics and Department of Applied Physics, Stanford University, CA 94305
[7]The Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA 94025
[8]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

I will review our work on lattice dynamics in the charge-density-wave (CDW) compounds *2H*-$NbSe_2$ [1], *1T*-$TiSe_2$ [2] and $TbTe_3$ [3]. Each of them is different with regard to the interplay of electronic structure and electron-phonon coupling properties. Nevertheless, all emphasize the general applicability of the stability criterion derived for a CDW by Chan & Heine [4].

$$\frac{4\eta_q^2}{\hbar\omega_{bare}} \geq \frac{1}{\chi_q} + \left(2\tilde{U}_q - \tilde{V}_q\right)$$

where η_q is the electron-phonon coupling associated with a mode at a bare energy of $\hbar\omega_{bare}$, χ_q is the dielectric response of the conduction electrons, and $\tilde{U}_q$ and $\tilde{V}_q$ are their Coulomb and exchange interactions. Although both sides of this inequality are essential in stabilizing the CDW order, the common assumption is that the modulation wave vector, $\vec{q}_{CDW}$, is determined by the right-hand side (i.e., by a singularity in the electronic dielectric function χq originating from a Fermi surface nesting).

Using high-energy resolution inelastic x-ray scattering and ab initio calculations of the lattice dynamical properties we analyzed the situation in the three above mentioned materials and find the following:

- There is no Fermi surface nesting in *2H*-$NbSe_2$ and $\boldsymbol{q}_{CDW}$ is completely defined by η_q.
- $TbTe_3$ features a weak nesting close to $\boldsymbol{q}_{CDW}$ but only including η_q yields the correct ordering wave vector.
- η_q in *1T*-$TiSe_2$ has a comparatively small wave vector dependence and the **q** dependence of one particular electronic scattering path defines $\boldsymbol{q}_{CDW}$.

[1] F. Weber, S. Rosenkranz, J.P. Castellan, R. Osborn, R. Hott, R. Heid, K.P. Bohnen, T. Egami, A.H. Said, and D. Reznik, *Physical Review Letters* **107** (10), 107403 (2011); F. Weber, R. Hott, R. Heid, K.P. Bohnen, S. Rosenkranz, J.P. Castellan, R. Osborn, A.H. Said, B.M. Leu, and D. Reznik, Physical Review B **87** (24), 245111 (2013).

[2] F. Weber, S. Rosenkranz, J.P. Castellan, R. Osborn, G. Karapetrov, R. Hott, R. Heid, K.P. Bohnen, and A. Alatas, *Physical Review Letters* **107** (26), 266401 (2011).

[3] M. Maschek, S. Rosenkranz, R. Heid, A. Said, P. Giraldo-Gallo, I.R. Fisher, and F. Weber, arXiv: cond-mat:1410.7592 (2014).

[4] S.K. Chan and V. Heine, *Journal of Physics F: Metal Physics* **3**, 795 (1973).

WK2

CDW and Electron-phonon Interaction in High-temperature Superconducting Cuprates

Matthieu Le Tacon

Max Planck Institute for Solid State Research, Stuttgart, 70569, Germany

I will present an overview of the results obtained from various x-ray scattering experiments on high temperature superconducting cuprates in the last couple of years. I will first focus on Cu L-edge resonant scattering experiments that led us to uncover charge density wave (CDW) correlations competing with superconductivity in the YBCO family [1–3], for which a complete temperature and doping dependent phase diagram has been worked out [4]. Further information was gained from high-resolution inelastic x-ray scattering that allows us to discuss the nature of the CDW. The observation of a quasi-elastic 'central peak' unraveled the static nature of the CDW correlations, attributed to the pining of CDW nanodomains on defects. Low energy phonons exhibit anomalously large superconductivity induced renormalizations close to the CDW ordering wave vector, providing new insights regarding the long-standing debate of the role of the electron-phonon interaction in the cuprates, a major factor influencing the competition between collective instabilities in correlated-electron materials [5].

[1] G. Ghiringhelli et al., *Science* **337**, 821 (2012).

[2] A. J. Achkar et al., *Phys. Rev. Lett.* **109**, 167001 (2012).

[3] S. Blanco-Canosa et al., *Phys. Rev. Lett.* **110**, 187001 (2013).

[4] S. Blanco-Canosa et al., *Phys. Rev. B* **90**, 054513 (2014).

[5] M. Le Tacon et al., *Nature Physics* **10**, 52 (2014).

WK2

Modeling the Phonon Dynamical Structure Factor S(Q,E) from First-principles Calculations: The Case Study of Thermoelectrics and Complex Oxides

Jiawang Hong, Jennifer Niedziela, Chen Li, Vickie Lynch, and Olivier Delaire

Oak Ridge National Laboratory, Oak Ridge, TN 37830

SimPhonies, a python-based application developed within CAMM at SNS, enables users to calculate the x-ray/neutron-weighted dynamical structure factor for phonon scattering, S(**Q**,E), from first-principles calculations. It enables direct, quantitative comparison with large datasets from inelastic x-ray/neutron scattering measurements on single-crystals. The SimPhonies code leverages first-principles electronic structure packages to calculate the x-ray/neutron scattering intensities convolved with instrumental resolution, including anharmonic effects, and outputs the scattering in the region of interest in reciprocal space. The benefits of reliable S(**Q**,E) simulations, and comparisons with measurements at HERIX/SNS, are illustrated with several scientific studies in a wide range of materials, including thermoelectrics, ferroelectrics and complex oxides.

Research was supported by the Center for Accelerating Materials Modeling from SNS data (CAMM), funded by the U.S. DOE, BES, MSED.

WK2

Clathrate Semiconductors: Novel, Open Framework, Crystalline Materials Based on Si, Ge, and Sn

Charles W. Myles and Dong Xue

Department of Physics, Texas Tech University, Lubbock, TX 79409

The Group IV elements Si, Ge, and Sn usually crystallize in the diamond lattice structure, which is the ground state phase for each. Less well-known is the fact that these elements can also form novel crystalline solids, called clathrates because of their structural similarities to clathrate hydrates. Group IV clathrates are metastable, expanded volume phases. As in the diamond structure, in the clathrates, the atoms are tetrahedrally coordinated in sp^3 covalent bonding configurations with their near-neighbors. In contrast to the diamond lattice, however, the clathrates contain pentagonal rings of atoms and their lattices are open frameworks containing large (20-, 24-, 28-atom) "cages". The two common clathrate varieties are Type I, a simple cubic lattice with 46 atoms per unit cell and Type II, a face centered cubic lattice with 34 atoms per unit cell. The cages can contain weakly bound impurities ("guests"), usually Group I or Group II atoms. A reason that the clathrates are interesting is that the choice of guest may be used to tune the material properties. The guests act as electron donors, but because of their weak bonding, they have only small effects on the host electronic band structures. However, they can vibrate with low frequency vibrational modes, which can strongly affect the vibrational properties. Some laboratory-synthesized, guest-containing clathrates show promise for thermoelectric applications precisely because the guests only weakly perturb the electronic properties, while strongly affecting the vibrational properties.

In this talk, the clathrates and their lattices will be introduced. The results of calculations of the properties of some Si, Ge and Sn-based Type I and Type II clathrates will then be presented. Where data is available, some results will be compared with experiments. Our calculations are motivated by experiments performed by G. Nolas and his group [1] at the U. of South Florida. Among the experimental techniques they have used to study the structural properties of these materials is powder x-ray diffraction (XRD). Our calculations have used a density-functional based, planewave, pseudopotential method. The results include equations of state, structural parameters, electronic bands, vibrational spectra, mean-square atomic displacements, and thermodynamic properties. Some recent results [2–5], obtained in collaboration with some present and former students will be discussed.

[1] M. Beekman, E.N. Nenghabi, K. Biswas, C. Myles, M. Baitinger, Y. Grin, and G.S. Nolas, *Inorganic Chemistry* **49**, 5338 (2010).

[2] Dong Xue and C. Myles, in preparation. See on-line March, 2015 APS Bulletin, papers F12-00007 and F12-00008.

[3] E.N. Nenghabi and C. Myles, *Phys. Rev.* B **77**, 205203 (2008); *Phys. Rev.* B **78**, 195202 (2008).

[4] K. Biswas, C. Myles, M. Sanati, and G. Nolas, *J. Appl. Phys.* **104**, 033535 (2008).

[5] P. Norouzzadeh, C. Myles, and D. Vashaee, *J. Appl. Phys.* **114**, 163509 (2013); *J. Alloys and Compounds* **587**, 474 (2014).

WK2

Comprehensive Scattering Studies of Microstructure, Anharmonic Phonons, and Thermodynamics near the Metal-insulator Transition in VO_2

J. D. Budai[1], J. Hong[1], O. Delaire[1], M. Manley[1], E. Specht[1], C. Li[1], J. Tischler[2], A. Said[2], B. Leu[2], D. Abernathy[1], A. Tselev[1], L. Boatner[1], and R. McQueeney[1]

[1]Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Argonne National Laboratory, Argonne, IL 60439

Vanadium dioxide is a strongly correlated material that exhibits a well-studied, but poorly understood, metal-insulator transition (MIT) coupled with a tetragonal (rutile) to monoclinic (M1) structural phase transition just above room temperature. Competing models for this coupled electronic and structural transition are based on either a Peierls MIT driven by instabilities in electron–lattice dynamics or a Mott MIT where strong electron–electron correlations drive charge localization. In spite of early predictions of a soft-mode lattice instability at the rutile R-point, phonon dispersions have not been measured in VO_2 because the incoherent neutron scattering cross-section precludes traditional single-crystal neutron scattering measurements. To shed light on changes in microstructure, lattice

dynamics, and thermodynamics in VO_2, we have combined a comprehensive set of x-ray and neutron scattering results with *ab initio* molecular dynamics calculations (AIMD). Four complementary scattering studies included: (1) x-ray microdiffraction at APS 33-BM, (2) single-crystal inelastic x-ray scattering studies of phonon dispersions at APS-HERIX, (3) inelastic neutron powder measurements of phonon density of states at SNS-ARCS, and (4) x-ray thermal diffuse scattering at APS 33-BM. We found good agreement between the experimental results and the AIMD predictions, and the calculations help reveal the physical mechanisms driving the MIT. Our results show, first, that previous proposals of a "soft mode" phase transition at a particular wavevector are incorrect. Second, we find that changes in the phonon spectra across the transition are responsible for most of the total entropy change, that is, the entropy change is dominated by vibrational rather than electronic contributions. Finally, we observe strongly anharmonic phonons across a wide region of reciprocal space in the tetragonal phase, and conclude that these short-lived, low-energy phonons are responsible for thermodynamically stabilizing the metallic phase at high temperatures.

Support by DOE Office of Basic Energy Sciences, Materials Sciences and Engineering Division; APS and SNS facilities supported by DOE-BES.

WK2

Critical Soft Modes and Negative Thermal Expansion

Jason Hancock

University of Connecticut, Storrs, CT 06269

We report a high resolution inelastic x-ray scattering study of phonons in a perovskite material which not only displays strong negative thermal expansion, but also exhibits a particularly stable high symmetry cubic phase down to 0.5 K. Our observations include a strong softening of a branch of excitations as the system is cooled, and strong signatures of critical fluctuations are apparent at the lowest temperatures measured. General aspects of the avoided ferroelastic phase boundary to a lower symmetry phase and the broad connection to the physics of perovskite materials will be discussed.

WK2

High-pressure Acoustic Phonons and Elasticity of Iron Alloys and Oxides

Jung-Fu Lin

Department of Geological Science, The University of Texas at Austin, Austin, TX 78712

Iron is the most abundant transition metal in the universe and also exists abundantly in the Earth's interior. Studying the physical and chemical properties of iron-bearing compounds, including Fe-Ni-Si alloys and oxides (e.g., magnetite, hematite, wustite), in extreme pressure-temperature environments are thus of great interest to deep-Earth mineral physicists as well as condensed matter physicists [1–3]. Due to the nature of the unfilled *3d* electronic orbitals, these compounds can potentially undergo a number of transitions in extreme conditions including structural, magnetic, spin-pairing, metallic, and/or charge-ordering. These transitions can significantly affect our understanding of the properties of these Fe-bearing compounds at high pressures. Since these compounds are opaque to visible lights, studying their elastic properties had been a challenge. In this presentation, I will highlight the use of the high-energy-resolution inelastic x-ray scattering (HERIX) technique coupled with a high-pressure diamond anvil cell at the Sector 3 and Sector 30 of the Advanced Photon Source to investigate the behavior of acoustic phonons and elasticity (full elastic tensors) of iron alloys and oxides at high pressures and/or temperatures. These experimental elasticity results, together with complimentary x-ray and laser spectroscopic measurements, are used to understand a number of outstanding questions in these systems including how the charge-ordering occurs in the mixed-valence magnetite at high pressure [1] and what are the alloying effects of light elements on the velocity profiles of iron in the deep-Earth core [2,3].

[1] J.F. Lin, J. Wu, J. Zhu, Z. Mao, A. H. Said, B. M. Leu, J. Cheng, Y. Uwatoko, C. Jin, and J. Zhou, Abnormal elastic and vibrational behaviors of magnetite at high pressures, *Scientific Reports* **2**, 6282, 2014.

[2] J. Liu, J.F. Lin, A. Alatas, and W. Bi, Sound velocities of bcc-Fe and $Fe_{0.85}Si_{0.15}$ alloy at high pressure and temperature, *Phys. Earth Planet. Inter.* **233**, 24–32, 2014.

[3] Z. Mao, J.F. Lin, J. Liu, A. Alatas, L. Gao, J. Zhao, and H.K. Mao, Sound velocities of Fe and Fe-Si alloys in the Earth's core, *Proc. Natl. Acad. Sci.* **109**, 10239–10244, 2012.

WK2

Looking for Hidden Phonons in URu_2Si_2

Nicholas Butch

NIST Center for Neutron Research, Gaithersburg, MD 20899

Among the outstanding problems in condensed matter physics, the identity of the order parameter in the hidden order phase of URu_2Si_2 is among the most conspicuous. I will discuss our recent x-ray and neutron study of the lattice, and inevitably, magnetic excitations in this material. I will highlight how HERIX measurements were essential to conclusively disentangle phonon dispersions from the magnetic excitations along certain directions. As a result, we have calculated directly the phonon contribution to the specific heat and analyzed the temperature dependence of the magnetic excitations. I will also present our measurement of phonons under pressure.